

## INFLUENCE OF THE TRANSPORT PROCESSES ON THE DYNAMIC CHARACTERISTICS OF A CONTINUOUS-FLOW CHEMICAL REACTOR\*

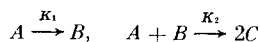
Iu.P. GUPALO, V.A. NOVIKOV and Iu.S. RIAZANTSEV

The dependence of the mean dynamic characteristics of a continuous-flow chemical reactor on the intensity of longitudinal stirring (Péclet number) in the presence of the quasistationary periodic perturbations in the reagent concentration at the reactor input is studied. The small perturbations method is used with the accuracy of up to the terms of third order of smallness for the case of a consecutively parallel chemical reaction, in the "weak" reaction approximation, to obtain an approximate analytic solution for the problem of concentration distribution in a one-dimensional, continuous-flow chemical reactor. The solution obtained is used to study the effect of the Péclet number on the mean characteristics of the reactor, namely on the degree of conversion, selectivity and yield. It is established that the presence of periodic variations in the initial reagent concentration can alter significantly the character of dependence of the mean degree of conversion on the intensity of the longitudinal stirring, as compared with the steady mode. The dependence of the Péclet number ensuring the maximum value of the mean degree of conversion on the reactor characteristics is obtained, and the characteristic domains of parameters variation in which the influence of the longitudinal transport on the dynamic behavior of the reactor is different, are found.

The interest shown in the study of nonsteady modes of continuous-flow chemical reactors is justified by the fact that, as was shown in a number of theoretical and experimental works, use of the forced periodic modes may lead to increase in the reactor performance efficiency compared with the steady mode /1-5/. The determination of optimal conditions for a reactor working in a nonsteady mode, requires solving of a number of problems connected with the study of the effect of the chemical reactor parameters on its dynamic characteristics. The expediency of such a formulation of the problem is justified by the fact that, as is shown below, the conditions for carrying out a chemical technological process which are optimal in the steady mode, are no longer optimal in the nonsteady mode. The intensity of the longitudinal stirring characterized by the Péclet number represents the parameter which effects significantly the performance of the chemical reactor. Study of the dependence of the mean dynamic characteristics on the Péclet number is the aim of this paper.

The authors of /6/ were the first to attempt the estimation of the effect of the transport processes in a tubular reactor on the magnitude of a nonsteady shift characterizing the deviation of the mean dynamic characteristics from their corresponding steady state values. Numerical methods were used to establish that for certain particular values of the defining parameters the longitudinal stirring increases the nonsteady shift. The shift attains its maximum value in a reactor with perfect stirring, and a minimum in a reactor with perfect displacement. Moreover, an analytic study of the dependence of the nonsteady shift on the Péclet number has shown /7/, in particular, that the regularity discovered numerically in /6/ is not universal and depends on the particular choice of the numerical values of the reactor parameters. The "weak" reaction approximation was used in /7/ to obtain an analytic criterion determined by the kinetic relationship and allowing the establishment of the manner in which the longitudinal stirring affects the nonsteady shift. In /8/ it was established that in certain cases the dependence of the nonsteady shift on the Péclet number can be nonmonotonous. Nonsteady modes in a tubular reactor at low Péclet numbers were investigated in /9/.

1. Formulation of the problem and approximate solution. Let us consider a one-dimensional model of a continuous-flow isothermal chemical reactor with longitudinal stirring. Let a consecutively parallel chemical reaction take place in the reactor according to the equation



\*Prikl. Matem. Mekhan., 46, No. 2, pp. 254-262, 1982

Using the dimensionless variables we can write the nonsteady equations, boundary and initial conditions for the concentration profiles of the components  $A$ ,  $B$  and  $C$  within the reactor, in the form

$$\begin{aligned}
 \frac{\partial c_A}{\partial t} &= \frac{1}{P} \frac{\partial^2 c_A}{\partial x^2} - \frac{\partial c_A}{\partial x} - (k_1' c_A + k_2' c_A c_B) & (1.1) \\
 \frac{\partial c_B}{\partial t} &= \frac{1}{P} \frac{\partial^2 c_B}{\partial x^2} - \frac{\partial c_B}{\partial x} - (k_2' c_A c_B - k_1' c_A) \\
 \frac{\partial c_C}{\partial t} &= \frac{1}{P} \frac{\partial^2 c_C}{\partial x^2} - \frac{\partial c_C}{\partial x} + 2k_2' c_A c_B \\
 x=0, & \quad -\frac{1}{P} \frac{\partial c_A}{\partial x} + c_A = c_{Af}(t), \quad -\frac{1}{P} \frac{\partial c_B}{\partial x} + c_B = 0, \\
 & \quad -\frac{1}{P} \frac{\partial c_C}{\partial x} + c_C = 0 \\
 x=1, & \quad \frac{\partial c_A}{\partial x} = \frac{\partial c_B}{\partial x} = \frac{\partial c_C}{\partial x} = 0 \\
 t=0, & \quad c_A(x, 0) = c_{Am}(x), \quad c_B(x, 0) = c_{Bin}(x), \quad c_C(x, 0) = c_{Cin}(x) \\
 c_A &= \frac{C_A}{C_{A0}}, \quad c_B = \frac{C_B}{C_{A0}}, \quad c_C = \frac{C_C}{C_{A0}}, \quad x = \frac{X}{L} \\
 P &= \frac{UL}{D}, \quad k_1' = \frac{K_1 L}{U}, \quad k_2' = \frac{K_2 LC_{A0}}{U}, \quad t = \frac{TU}{L}
 \end{aligned}$$

Here  $X$  is the spatial coordinate ( $0 \leq X \leq L$ ),  $L$  is the reactor length,  $T$  is time,  $C_A$ ,  $C_B$ ,  $C_C$  are the components concentration in the reactor,  $C_{Af}$  is the concentration of the reacting species at the reactor input,  $C_{A0}$  is the steady state value of the concentration  $C_{Af}$ ,  $U$  is the rate of reagent supply,  $D$  is the effective diffusion coefficient,  $K_1$  and  $K_2$  are the chemical reaction rate constants and  $P$  is the Péclet number. We assume that the concentration of the reagent  $A$  at the reactor input is a periodic function of time, and its mean value over a single period is equal to its steady state value, i.e.  $\langle c_{Af}(t) \rangle = 1$ .

Performing certain additions, we obtain from (1.1)

$$\begin{aligned}
 \frac{\partial c}{\partial t} &= \frac{1}{P} \frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial x} & (1.2) \\
 x=0, & \quad -\frac{1}{P} \frac{\partial c}{\partial x} + c = c_{Af}(t); \quad x=1, \quad \frac{\partial c}{\partial x} = 0 \\
 t=0, & \quad c(x, 0) = c_{in}(x), \quad c = c_A + c_B + c_C
 \end{aligned}$$

In what follows, we shall concern ourselves only with the periodic steady state solutions independent of the form of the initial distribution. Averaging over a period, we obtain from (1.2) the following expression for the steady state mode:

$$\langle c_A \rangle + \langle c_B \rangle + \langle c_C \rangle = 1 \quad (1.3)$$

Let us introduce the following average quantities:  $\langle \xi \rangle = 1 - \langle c_A \rangle$  is the degree of reagent conversion,  $\langle s_B \rangle = \langle c_B \rangle / \langle \xi \rangle$ ,  $\langle s_C \rangle = \langle c_C \rangle / \langle \xi \rangle$  is the selectivity referred to the products, and  $\langle \eta_B \rangle = \langle c_B \rangle$ ,  $\langle \eta_C \rangle = \langle c_C \rangle$  are the product yields. We shall determine the reactor characteristics averaged over time in the presence of periodic perturbations in the reagent concentration  $A$  at the reactor input, and investigate the dependence of these characteristics on the reactor parameters, in particular on the transport processes characterized by the Péclet number. From (1.3) it follows that  $\langle \xi \rangle = \langle \eta_B \rangle + \langle \eta_C \rangle$ ,  $\langle s_B \rangle + \langle s_C \rangle = 1$ , therefore from now on we shall only consider the first two equations of the system (1.1).

We shall solve the problem (1.1) in the "weak" chemical reaction approximation, assuming that the dimensionless chemical reaction rates are small, i.e.  $k_1' = \varepsilon k_1 = O(\varepsilon)$ ,  $k_2' = \varepsilon k_2 = O(\varepsilon)$ ,  $\varepsilon \ll 1$ . We shall limit ourselves to the quasistationary periodic perturbations assuming that the function  $c_{Af}(t)$  varies little over the period comparable with the characteristic time during which the reagent remains within the reactor. Seeking the solution of (1.1) in the form of a series in powers of  $\varepsilon$  accurate to within terms of third order of smallness, we obtain the following expression for the quasistationary distribution of concentration in the reactor:

$$\begin{aligned}
 c_A(x, t) &= c_{A0} - \varepsilon k_1 c_{A0} \Omega_0(P, x) - \varepsilon^2 k_1 (k_2 c_{A0}^2 - k_1 c_{A0}) \times & (1.4) \\
 & \quad \Omega(P, x) + \varepsilon^3 \{ [k_1^2 (k_2 c_{A0}^2 - k_1 c_{A0}) + k_1 k_2 (k_2 c_{A0}^3 + \\
 & \quad k_1 c_{A0}^2)] \Omega_1(P, x) + k_1^2 k_2 c_{A0}^2 \Omega_2(P, x) \} + O(\varepsilon^4) \\
 c_B(x, t) &= \varepsilon k_1 c_{A0} \Omega_0(P, x) - \varepsilon^2 k_1 (k_2 c_{A0}^2 + k_1 c_{A0}) \Omega(P, x) + \\
 & \quad \varepsilon^3 \{ [k_1^2 (k_1 c_{A0} - k_2 c_{A0}^2) + k_1 k_2 (k_2 c_{A0}^3 + k_1 c_{A0}^2)] \Omega_1(P, x) + \\
 & \quad k_1^2 k_2 c_{A0}^2 \Omega_2(P, x) \} + O(\varepsilon^4)
 \end{aligned}$$

$$\begin{aligned}
c_{A0} &= c_{Af}(t), \quad \Omega_0(P, x) = x + \frac{1 - e^{-P(1-x)}}{P} \\
\Omega(P, x) &= \frac{e^{-P} - 3e^{-P(1-x)} + 2}{P^2} + \frac{2x - 2e^{-P(1-x)} + xe^{-P(1-x)}}{P} + \frac{x^2}{2} \\
\Omega_1(P, x) &= \frac{4e^{-P}}{P^3} (1 - e^{Px}) + \frac{e^{-P}}{P^2} (2 - x - xe^{Px}) + \frac{x^2}{P} + \\
&\quad \frac{x^3}{6} + \left[ \frac{5 + e^{-P}}{P^3} (e^{-Px} - e^{-P}) + \frac{e^{-P}}{P} \left( \frac{3}{P} - 2 \right) (x - 1) - \right. \\
&\quad \left. \frac{5}{P^2} (xe^{-Px} - e^{-P}) + \frac{x^2}{2P} (e^{-Px} - e^{-P}) - \frac{e^{-P}}{2P} (x^2 - 1) \right] e^{Px} \\
\Omega_2(P, x) &= \frac{e^{-2P}}{2P^3} (e^{2Px} - 1) - \frac{e^{-P}}{P^2} e^{Px} + \frac{x^2}{P} + \frac{x^3}{3} + \\
&\quad \left[ \frac{5}{P^3} (e^{-Px} - e^{-P}) - \frac{e^{-2P}}{P^3} (e^{Px} - e^P) + \frac{5}{P^2} (xe^{-Px} - e^{-P}) - \right. \\
&\quad \left. \frac{1}{P} (x^2 e^{-Px} - e^{-P}) + \frac{e^{-P}}{P} (x^2 - 1) \right] e^{Px}
\end{aligned}$$

2. Influence of the longitudinal dispersion. The approximate analytic solution of the problem obtained above enables us to investigate the dependence of the mean dynamic characteristics of the reactor on the magnitude of the longitudinal dispersion in the reactor (on the Péclet number). Using the expressions (1.4) for the mean values of the degree of conversion, selectivity and yield, we obtain

$$\langle \xi \rangle = \varepsilon k_1 + \varepsilon^2 k_1 \langle (k_2 c_{A0}^2 - k_1 c_{A0}) \rangle \Omega(P) - \varepsilon^3 \{ [k_1^2 \langle k_2 c_{A0}^2 - k_1 c_{A0} \rangle + k_1 k_2 \langle k_2 c_{A0}^3 + k_1 c_{A0}^2 \rangle] \Omega_1(P) + k_1^2 k_2 \langle c_{A0}^2 \rangle \Omega_2(P) \} + O(\varepsilon^4) \quad (2.1)$$

$$\begin{aligned}
\langle s_B \rangle &= 1 - 2\varepsilon k_2 \langle c_{A0}^2 \rangle \Omega(P) + O(\varepsilon^2) \\
\langle s_C \rangle &= 2\varepsilon k_2 \langle c_{A0}^2 \rangle \Omega(P) + O(\varepsilon^2) \\
\langle \eta_B \rangle &= \varepsilon k_1 - \varepsilon^2 k_1 \langle k_2 c_{A0}^2 + k_1 c_{A0} \rangle \Omega(P) + O(\varepsilon^3) \\
\langle \eta_C \rangle &= 2\varepsilon^2 k_1 k_2 \langle c_{A0}^2 \rangle \Omega(P) + O(\varepsilon^3)
\end{aligned} \quad (2.2)$$

where

$$\begin{aligned}
\Omega(P) &\equiv \Omega(P, 1) = \frac{e^{-P} - 1}{P^2} + \frac{1}{P} + \frac{1}{2} \\
\Omega_1(P) &\equiv \Omega_1(P, 1) = \frac{4(e^{-P} - 1)}{P^3} + \frac{3e^{-P} + 1}{P^2} + \frac{1}{P} + \frac{1}{6} \\
\Omega_2(P) &\equiv \Omega_2(P, 1) = \frac{1 - e^{-2P}}{2P^3} - \frac{1}{P^2} + \frac{1}{P} + \frac{1}{3}
\end{aligned}$$

Clearly, the dependence of the initial reactor characteristics on the longitudinal stirring intensity is determined by the functions  $\Omega(P)$ ,  $\Omega_1(P)$ ,  $\Omega_2(P)$ . Operating the reactor in the nonsteady mode leads to an increase in the mean values of the degree of reagent conversion, selectivity and yield of the product  $C$ , and to a decrease in the mean values of the selectivity and yield of the product  $B$ . Analyzing the expressions (2.2) we can conclude that the character of the dependence of the selectivity and yield on the Péclet number does not change when the reactor operation passes from the steady to the nonsteady mode, i.e. the optimal level of stirring (Péclet number) in the steady mode remains, for these characteristics (selectivity and yield) optimal also in the nonsteady mode. This conclusion however is not true for the mean degree of conversion.

Let us investigate this problem in more detail. We can assume without loss of generality that  $c_{Af}(t) = 1 + \varphi(t)$ , and  $\varphi(1) \geq -1$ ,  $\langle \varphi(t) \rangle = 0$ . Then from (2.1) we obtain, with the accuracy of up to the second order terms in  $\varepsilon$ ,

$$\begin{aligned}
\langle \xi \rangle &= \varepsilon k_1 + \varepsilon^2 \Delta(k_1, k_2; \sigma) \Omega(P) + O(\varepsilon^3) \\
\Delta(k_1, k_2; \sigma) &= k_1 [k_2 (1 + \sigma^2) - k_1], \quad \sigma^2 = \langle \varphi(t)^2 \rangle \\
\Delta \xi &\equiv \langle \xi \rangle - \xi_s = \varepsilon^2 k_1 k_2 \sigma^2 \Omega(P) + O(\varepsilon^3)
\end{aligned} \quad (2.3)$$

where  $\Delta \xi$  is the nonsteady shift in the degree of conversion caused by periodic variation in the reagent concentration at the reactor input, and  $\xi_s$  is the degree of conversion in the steady mode. From (2.3) and (2.4) it follows that in the presence of the perturbations in the initial concentration, the dispersion  $\sigma^2 = \langle \varphi^2 \rangle$  exerts direct influence on the magnitude of the mean degree of conversion ( $\sigma$  is the mean square deviation). We see that the term of first order in  $\varepsilon$  of (2.3) is independent of the Péclet number, therefore further terms must be taken into account in the course of examining the dependence of the mean degree of conversion on the

longitudinal stirring intensity.

Analyzing the second order terms in  $\varepsilon$  of (2.3) we see that the character of the dependence of the degree of conversion on the Péclet number is governed by the sign of the expression  $\Delta(k_1, k_2, \sigma)$ , since the function  $\Omega(P)$  decreases monotonously. Thus the three-dimensional space of parameters  $(k_1, k_2, \sigma)$  is split by the surface  $\Delta(k_1, k_2, \sigma) = 0$  into two regions in which the longitudinal stirring has different effect on the magnitude of the mean degree of conversion. This enables us to indicate, at every point of the  $(k_1, k_2, \sigma)$ -parameter space, the optimal Péclet number which ensures the maximum mean degree of conversion in the reactor. From (2.3) we see that the sign of the function  $\Delta$  depends on two parameters only, namely on  $k_1/k_2$  and  $\sigma$ . This enables us to carry out the analysis on the plane  $(k_1'/k_2', \sigma)$ , shown in Fig.1. The parabola  $\Delta = 0$  divides the plane into two regions. When  $\Delta > 0$  ( $k_1'/k_2' < 1 + \sigma^2$ ) the mean degree of

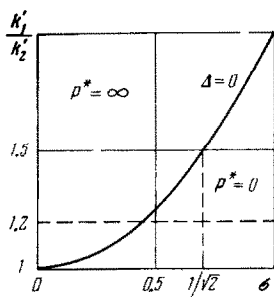


Fig.1

conversion increases monotonously with the increasing longitudinal stirring intensity (diminishing Péclet number) and reaches its maximum value in the reactor with perfect stirring ( $P^* = 0$ ). When  $\Delta < 0$  ( $k_1'/k_2' > 1 + \sigma^2$ ), the mean degree of conversion increases monotonously with decreasing longitudinal stirring intensity (increasing Péclet number) and reaches its maximum value in a reactor with perfect displacement ( $P^* = \infty$ ). We note that in the steady mode ( $\sigma = 0$ ) the character of the effect of the longitudinal dispersion on the mean degree of conversion is governed by the sign of the expression  $1 - k_1'/k_2'$ . Thus if the values of the dimensionless rate constants are such that  $k_1'/k_2' > 1$ , then the passage from the steady to the nonsteady mode of operation will be accompanied by a change in the manner in which the longitudinal stirring affects the mean degree of conversion at some value of the perturbation dispersion (the sign of the derivative  $d\langle\xi\rangle/dP$  will change). This will lead to the change in the type of the optimal reactor. In the steady mode the reactor with perfect displacement ( $P^* = \infty$ ) is optimal, and in the nonsteady mode it is the reactor with perfect stirring ( $P^* = 0$ ) that is optimal.

If on the other hand  $k_1'/k_2' < 1$ , then the passage from the steady to the nonsteady mode will not affect the character of the effect of the longitudinal stirring on the mean degree of conversion and the optimal reactor type ( $P^* = 0$ ) will remain the same.

The results obtained lead to conclusion that a chemical reactor with an optimal level of longitudinal stirring in the steady mode is, generally speaking, not optimal under the non-steady conditions.

We illustrate the results obtained by considering two particular cases in which the dependence of the initial concentration of the reagent  $A$  is defined in specific terms. Let the initial concentration vary according to the harmonic law  $\varphi(t) = g \sin \omega t$ ,  $0 \leq g \leq 1$ . Then  $\sigma = g/\sqrt{2}$ ,  $0 \leq \sigma \leq 1/\sqrt{2}$ . The results obtained above enable us to reach the following conclusions regarding the effect of the perturbation amplitude  $g$  on the character of the dependence of the mean degree of conversion on the longitudinal stirring (see Fig.1 where the point  $\sigma = 1/\sqrt{2}$  corresponds to the maximum possible perturbation amplitude). If  $k_1'/k_2' \notin [1; 1.5]$ , then the perturbations in the initial concentration do not affect the character of the dependence of the mean degree of conversion on the Péclet number, i.e. the sign of the derivative  $d\langle\xi\rangle/dP$  does not depend on the amplitude  $g$ . If  $k_1'/k_2' \in [1; 1.5]$ , then at certain value of the perturbation amplitude the character of the effect of the longitudinal stirring on the mean degree of conversion will change, i.e. the derivative  $d\langle\xi\rangle/dP$  will change its sign, and so will the type of reactor ensuring the maximum degree of conversion. Thus the perturbation amplitude can influence significantly the character of the dependence of the mean degree of conversion on the Péclet number.

As the second example we consider a periodic step-wise, dependence of the initial concentration on time

$$\varphi(t) = \begin{cases} \varphi_+, & 0 \leq t < \gamma T_1 \\ -\varphi_-, & \gamma T_1 \leq t < T_1 \end{cases} \quad (2.5)$$

Here  $T_1$  is the period of the function  $\varphi(t)$ ,  $\gamma$  is a fraction of the period, and  $\varphi_+, \varphi_- \geq 0$ . Using the condition  $\langle\varphi\rangle = 0$  we can obtain from (2.5)  $\sigma^2 = \langle\varphi^2\rangle = \varphi_+\varphi_-$ . It is clear that in this case the dispersion may vary over the interval  $[0, \infty]$ . Therefore if  $k_1'/k_2' > 1$ , then a function of the type (2.5) exists such that the passage from the steady to the nonsteady mode of operation is accompanied by the change in the sign of the derivative  $d\langle\xi\rangle/dP$ , and hence also in the type of the reactor ensuring the maximum degree of conversion. If on the other hand  $k_1'/k_2' < 1$ , then the change to the nonsteady mode does not produce a qualitative change in the character of the relation  $\langle\xi\rangle(P)$ .

The case when the values of  $\Delta$  are nearly zero requires a special treatment in which the

expression for the mean degree of conversion must be analyzed with the accuracy of up to the terms of third order in  $\varepsilon$ . Let us consider the neighborhood of the curve  $\Delta = 0$ . Let  $\Delta/k_1 = b\varepsilon$ ,  $b = O(1)$ . Expanding the coefficients of (2.1) into a Taylor series in powers of  $\varepsilon$  we obtain the following expression for the arbitrary variation in the reagent concentration at the reactor input  $c_{Af}(t) = 1 + \varphi(t)$ :

$$\begin{aligned} \langle \xi \rangle &= \varepsilon k_1 + \varepsilon^3 k_1^3 \Omega_3(P, \beta, \alpha) + O(\varepsilon^4) \\ \Omega_3(P, \beta, \alpha) &= \beta \Omega(P) - \alpha \Omega_1(P) - \Omega_2(P) \\ \beta &= \frac{b}{k_1^2} \equiv \frac{k_2'(1 + \langle \varphi^2 \rangle) - k_1'}{(k_1')^2}, \quad \alpha = \frac{1 + 3\langle \varphi^2 \rangle + \langle \varphi^3 \rangle}{(1 + \langle \varphi^2 \rangle)^2} + 1 \end{aligned} \quad (2.6)$$

We note that the expression (2.6) can be obtained by direct solution of the problem (1.1) with the parameters chosen appropriately. We see from (2.6) that the effect of the longitudinal stirring on the mean degree of conversion is determined by the relation  $\Omega_3(P, \beta, \alpha)$  where  $\beta$  and  $\alpha$  are regarded as parameters. Depending on the values of these parameters, the function  $\Omega_3(P)$  may be monotonously decreasing, monotonously increasing, or have a maximum.

The optimal Péclet number  $P^*$  ensuring the maximum mean degree of conversion is a function of a point on the parametric  $(\alpha, \beta)$ -plane. The surface  $P^* = P^*(\alpha, \beta)$  can be defined using (2.6) by the following implicit equation:

$$\frac{\partial \Omega_3}{\partial P} \equiv \beta \Omega'(P^*) - \alpha \Omega_1'(P^*) - \Omega_2'(P^*) = 0 \quad (2.7)$$

The isolines on the surface  $(\alpha, \beta)$  corresponding to the fixed value of the value Péclet number (intersection of the surface (2.7) by the planes  $P = \text{const}$ ) are straight lines, the equations of which are obtained from (2.7)

$$\begin{aligned} \beta - \alpha m(P) + n(P) & \quad (2.8) \\ m(P) &= \frac{\Omega_1'}{\Omega'} = \left\{ \frac{1}{P} \left[ \frac{12}{P} (e^{-P} - 1) + 10e^{-P} + 2 \right] + 3e^{-P} + 1 \right\} \left[ \frac{2}{P} (e^{-P} - 1) + e^{-P} + 1 \right]^{-1} \\ n(P) &= \frac{\Omega_2'}{\Omega'} = \left\{ 1 - \frac{1}{P} \left[ \frac{3}{2P} (e^{-2P} - 1) + e^{-2P} + 2 \right] \right\} \times \left[ \frac{2}{P} (e^{-P} - 1) + e^{-P} + 1 \right]^{-1} \end{aligned}$$

Thus the surface  $P^* = P^*(\alpha, \beta)$  is a ruled surface. Setting any value of the Péclet number and using the explicit expression for the functions  $m(P)$  and  $n(P)$ , we obtain the coefficients for the equations (2.8) of the isolines. Fig. 2 depicts the relationships for  $m(P)$  and  $n(P)$ , and we see that these functions are monotonously decreasing and vary over the interval  $1 < m, n < 2$ . Fig. 3 shows the isolines (2.8) for various values of the Péclet number. We see that they divide the parametric  $(\alpha, \beta)$ -plane into three characteristic regions and do not intersect when  $\alpha > 0$ . In the region  $\beta > 2(\alpha + 1)$  the function  $\Omega_3(P)$  is monotonously decreasing, therefore the longitudinal stirring increases the mean degree of conversion and the maximum mean degree of conversion is attained in a reactor with perfect stirring ( $P^* = 0$ ). In the region  $\beta < \alpha + 1$  relation  $\Omega_3(P)$  increases monotonously, therefore the longitudinal stirring reduces

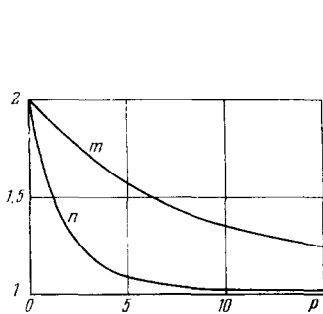


Fig. 2

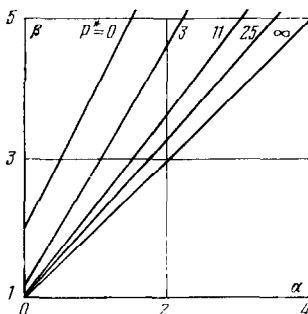


Fig. 3

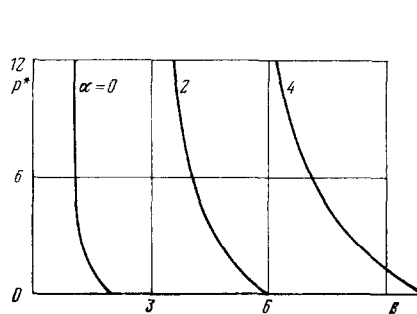


Fig. 4

the mean degree of conversion and the maximum mean degree of conversion is attained in a reactor with perfect displacement ( $P^* = \infty$ ). In the region  $\alpha + 1 < \beta < 2(\alpha + 1)$   $\Omega_3(P)$  is not monotonous, has a maximum and the longitudinal stirring can therefore reduce, or increase (depending on the Péclet number) the mean degree of conversion. The maximum mean degree of

conversion is reached in the reactor with intermediate level of stirring ( $0 < P^* < \infty$ ) and the Péclet number corresponding to the optimal stirring level lies on the surface (2.7).

Fig.4 depicts the surface (2.7) intersected by the plane  $\alpha = \text{const}$ , for various values of  $\alpha$ . We note that the case  $\alpha = 2$  corresponds to the steady mode ( $\varphi(t) \equiv 0$ ) and the case  $\alpha = 0$  to the autocatalytic reaction discussed in /10/.

From (2.6) we see that to find the parameters  $\alpha$  and  $\beta$  which determine the character of the relation connecting the mean degree of conversion and the Péclet number, we must know four quantities:  $k_1', k_2', \langle \varphi^2 \rangle$  and  $\langle \varphi^3 \rangle$ . The first two quantities are obtained from the chemical kinetics, and the last two are functionals of the perturbation in the initial reagent concentration. The dispersion  $\sigma^2 = \langle \varphi^2 \rangle$  characterises the spread of the initial concentration about the mean steady value, and the third moment  $\langle \varphi^3 \rangle$  characterizes the degree of symmetry of the initial concentration perturbations relative to its mean value. Thus the spread and the degree of symmetry of the input perturbations affect significantly the dependence of the mean degree of conversion on the longitudinal stirring intensity.

As an example, we shall consider a periodic step-wise dependence of the input concentration on time (2.5). We have

$$\langle \varphi^3 \rangle = \varphi_+ \varphi_- (\varphi_+ - \varphi_-) \equiv \langle \varphi^3 \rangle (\varphi_+ - \varphi_-) \quad (2.9)$$

Analyzing Fig.3 and the expression (2.9), we can conclude that in this case the variation in the symmetry of the input concentration perturbation (value of  $\langle \varphi^3 \rangle$ ) can lead to a change in the character of the dependence of the mean degree of conversion on the Péclet number, although the spread of the perturbations ( $\langle \varphi^2 \rangle$ ) may still remain unchanged.

In the case of symmetric perturbations  $\langle \varphi^3 \rangle = 0$  (the harmonic perturbations or the step-wise perturbations at  $\varphi_+ = \varphi_-$  can serve as examples) and the position of the point in the parametric  $(\alpha, \beta)$ -plane is determined by the following three parameters only:  $k_1', k_2', \sigma^2$ . Fig.5 shows the relationships  $(\alpha(\sigma), \beta(\sigma))$  for fixed values of the reaction rate constants  $k_1'/k_2' = 1, 2; k_1' = 0.03$  for the mean square deviation  $\sigma$  varying over the interval  $[0, 1]$  (curve I) and isoline  $P^* = \text{const}$ . The arrow on curve I shows the direction in which the parameter  $\sigma$  increases. Fig.1 shows, for comparison, the straight line  $k_1'/k_2' = 1, 2$ , by means of dashes. We see that curve I has three characteristic segments. On the segment DM the mean degree of conversion increases monotonously with increasing Péclet number and attains its maximum value in the reactor with perfect displacement. Point D corresponds to the value  $\sigma = 0$  and the value of  $\sigma_\infty$  at the point M is given by the equation

$$\beta(\sigma) = \alpha(\sigma) + 1$$

On the segment MN the mean degree of conversion passes through a maximum at a finite value of the Péclet number, assuming its maximum value in a reactor with intermediate stirring level. The optimal Péclet number is determined by the intersection of curve I with the corresponding isoline, and the value  $\sigma_0$  at the point N is given by the equation

$$\beta(\sigma) = 2[\alpha(\sigma) + 1]$$

On the segment NR the mean degree of conversion decreases monotonously with increasing Péclet number and assumes its maximum value in a reactor with perfect stirring. The point R corresponds to the value  $\sigma = 1$ . We note that the point S on curve I has the corresponding value of  $\sigma = 1/\sqrt{2}$  which corresponds to the maximum amplitude of the sinusoidal perturbations. At the point R we gave  $\sigma = 1$ , which corresponds to the maximum amplitude of the symmetrical, step-wise perturbations. Thus, depending on the magnitude of the mean square deviation of the input concentration perturbations from its mean value, we can have three different situations. The reactor with perfect displacement is optimal for  $0 \leq \sigma \leq \sigma_\infty$ , the reactor with intermediate stirring level for  $\sigma_\infty < \sigma < \sigma_0$  and the reactor with perfect stirring is optimal for  $\sigma_0 \leq \sigma \leq 1$ . In the general case the optimal Péclet number  $P^*$  is a function of four parameters:  $k_1', k_2', \sigma, \langle \varphi^3 \rangle$ . The equation of the level surfaces  $P^*(k_1', k_2', \sigma, \langle \varphi^3 \rangle) = \text{const}$  can be obtained from (2.6)–(2.8). Fig.6 shows, as an example, the intersections of the level surface  $P^*(k_1', k_2', \sigma, 0) = 0$  by the planes  $\sigma = \text{const}$  and this gives some idea of the configurations of the level surfaces for the case of symmetrical perturbations.

Thus the analysis carried out in the weak chemical reaction approximation indicates a complex dependence of the mean dynamic characteristics on the Péclet number. The reactor characteristics together with the functionals of the input perturbations serve as the defining parameters, and the presence of periodic perturbations in the reagent concentration at the chemical reactor input can change fundamentally the character of the relation connecting the mean dynamic reactor characteristics and the longitudinal stirring intensity, as compared with the steady mode of the process. This suggests that the analysis of the steady modes turns out to be insufficient for solving the problem concerning the advisability of choosing one or another type of the chemical reactor by means of mathematical modelling.

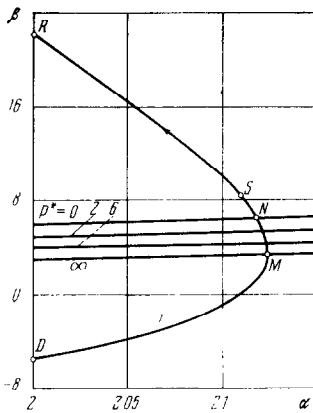


Fig.5

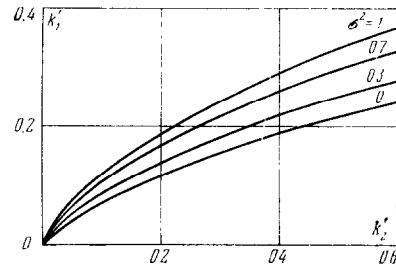


Fig.6

## REFERENCES

1. DOUGLAS J.M. and RIPPIN D.W.T., Unsteady state process operation. Chem. Engng. Sci., Vol. 21, No.4, 1966.
2. BAILEY J.E., Periodic operation of chemical reactors: a review. Chem. Engng. Commun. Vol. 1, No.3, 1973.
3. AL-TAIE A.S. and KERSHENBAUM L.S., Effect of periodic operation on the selectivity of catalytic reactions. In: 5-th Internat. Symposium Chem. React. Engng, Houston, Tex., 1978, Washington, Amer. Chem. Soc. 1978.
4. LEE C.K. and BAILEY J.E., Modification of consecutive-competitive reaction selectivity by periodic operation. Industr. Engng.Chem. Process Design Developm., Vol.19, No.1, 1980.
5. LEE C.K., YEUNG S.Y.S. and BAILEY J.E., Experimental studies of a consecutive-competitive reaction in steady state and forced periodic CSTRs. Canad. J. Chem. Engng, Vol.58, No.2, 1980.
6. LANNUS A. and KERSHENBAUM L.S., On the cyclic operation of tubular reactors, AIChE Journal, Vol.16, No.2, 1970.
7. GUPALO Iu.P., NOVIKOV V.A. and RIAZANTSEV Iu.S., Effect of longitudinal dispersion on the dynamic characteristics of a continuous-flow chemical reactor. PMM Vol.44, No.3, 1980.
8. GUPALO Iu.P., NOVIKOV V.A. and RIAZANTSEV Iu.S., Continuous-flow system with fractional order chemical reaction in the presence of axial dispersion. PMM Vol.45, No.2, 1981.
9. NOVIKOV V.A., On unsteady modes of operation of an isothermal reactor with longitudinal mixing. PMM Vol.43, No.3, 1979.
10. GUPALO Iu.P., NOVIKOV V.A. and RIAZANTSEV Iu.S., Effect of longitudinal stirring on the degree of conversion of the reagent in a continuous-flow system. Izv. Akad. Nauk SSSR, MZhG, No.2, 1981.

Translated by L.K.